

Carbonate as Sputter Target Material for Rapid ^{14}C AMS

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1. Abstract

This paper describes a technique for measuring the ^{14}C content of carbonate samples by producing C^- ions directly in the negative ion sputter source of an accelerator mass spectrometer (AMS) system. This direct analysis of carbonate material eliminates the time and expense of graphite preparation. Powdered carbonate is mixed with titanium powder, loaded into a target cartridge, and compressed. Beam currents for optimally-sized carbonate targets (0.09-0.15 mg C) are typically 10-20% of those produced by optimally-sized graphite targets (0.5-1 mg C). Modern ($>0.8 \text{ Fm}$) samples run by this method have standard deviations of 0.009 Fm or less, and near-modern samples run as unknowns agree with values from traditional hydrolysis/graphite to better than 2%. Targets with as little as 0.06 mg carbonate produce useable ion currents and results, albeit with increased error and larger blank. In its current state, direct sputtering is best applied to problems where a large number of analyses with lower precision are required. These applications could include age surveys of deep-sea corals for determination of historic population dynamics, to identify samples that would benefit from high precision analysis, and for growth rate studies of organisms forming carbonate skeletons.

1. Introduction

Radiocarbon provides a tool for direct dating of carbon-containing materials from the last fifty thousand years and is also used in a wide range of fields to trace the rate and amplitude of processes in which carbon is involved. While the details of sample preparation for solid-source accelerator mass spectrometry (AMS) vary, all methods oxidize samples to CO₂ and then reduce this CO₂ to graphite before analysis [1]. This process is labor-intensive and introduces background contamination through sample handling. These two issues impose limits on the minimum sample size and on sample preparation efficiency. In this study, we investigate the feasibility of using calcium carbonate as a direct carbon source for AMS in order to eliminate some of the problems associated with traditional sample preparation. This method could change the way that carbonate radiocarbon analyses are used in ocean and earth sciences.

In the past, most projects have had to select a small subset of samples for AMS analysis due to prohibitively high per-analysis costs. The cost and labor savings with a faster and less expensive method could lead to a new, multi-sample, “survey-mode” analysis strategy. For example, several cruises have collected thousands of fossil deep-sea corals from the North Atlantic and Southern Oceans [2,3], but dating all of these samples to examine the temporal population dynamics, or even to identify samples suitable for paleoclimate studies can be costly and time consuming using either the decay of uranium to thorium, or graphite ¹⁴C hydrolysis methods. Applied to fossil deep-sea corals, rapid, inexpensive analysis of hundreds of samples would add new insights into our understanding of coral population dynamics and their past bio-geography. “Survey-

mode” analysis could also be beneficial to studies that seek to produce first-pass chronologies of sediment cores or to survey the age of core-top sediments. A second potential advantage to a direct sputter method is a reduction in required sample mass. At the moment AMS labs typically request samples containing roughly 10 mg of carbonate to make an analysis. Traditional small- or ultra-small sample AMS can analyze graphite targets containing 25 to 100 $\mu\text{g C}$ or 2 to 25 $\mu\text{g C}$, respectively, both at reduced accuracy and precision [4-6]. Assuming 100% yield from a carbonate sample, this would require 16 to 833 μg of carbonate. Reducing the minimum sample size for routine analysis would allow higher resolution studies of continuous records of the history of radiocarbon (e.g. speleothems or coral samples) and may also open up new areas of study, for example dating of single foraminifera in marine sediment cores (figure 1b). Dating multiple single foraminifera would put direct constraints on age biases and produce new insights into the rates and depths of smoothing by bioturbation.

Carbon ions for traditional solid-source AMS are produced by sputtering a mixture of graphite and iron with Cs^+ ions. Ions including C^- are produced and extracted using an electrical potential [7]. Negative ions may also be produced by a Cs sputter source from CO_2 gas introduced onto and retained on a titanium frit at the sputtering location [8,9]. Performance of these hybrid gas ion sources is related to the gettering potential of the metal used for the sputtering surface [10], and the shape of this surface [11,12]. These gas ion sources are assumed to work by adsorption of CO_2 onto the titanium surface followed by breakup and ionization caused by sputtering by the Cs^+ beam [13].

2. Methods

Targets for carbonate sputtering were made by mixing carbonate powder with a metal powder (usually titanium) and loading this mixture into a pre-drilled hole in a front loaded aluminum cartridge. Samples were compressed in the cartridge using a hammer and steel pin. Additional titanium was added on top of samples and again compressed to form a porous sputtering surface. We refer to this additional titanium as a “cap” or a “frit” throughout the paper.

2.1. Carbonate samples

For developing and testing the carbonate sputtering method, we used a range of carbonate-containing materials (table I). These samples were chosen to span a wide range of Fm, from radiocarbon-dead to -modern. All sample types have been analyzed via AMS using the traditional hydrolysis-graphite technique [14], and several are well quantified as common secondary standards for AMS. Several samples come from a suite of deep-sea corals that have been dated using traditional hydrolysis, combustion via an elemental analyzer [3] and also direct analysis of CO₂ produced by hydrolysis in phosphoric acid *via* a gas ion source [15]. Using these samples has provided an immediate comparison of the accuracy, quality and cost of the direct sputtering method compared to the standard hydrolysis graphite technique as well as allowing comparison with several alternate techniques currently in development.

In keeping with rapid, low-cost analysis, the sample preparation was kept as simple as possible. Corals were cut, physically cleaned, and then rinsed with methanol to remove possible organic contamination, while mineral carbonate samples were left

untreated. Samples were then ground to a coarse powder (approximately 100 mesh) with a small agate mortar and pestle.

2.2. Catalyst / getter powders

Initial tests determined that carbonate targets require metal powder mixed with the carbonate sample to produce appreciable currents. Titanium and iron powders in different grain sizes (100 and 325 mesh) were tested. We also measured performance of targets with and without a 0.5 mg titanium “cap” or “frit” (as discussed earlier) added to the front surface of the target. All metal powders were cleaned and activated before preparing each batch of samples by baking in vacuum at 800°C for 4 hours.

2.3. Target preparation

Three methods were investigated for the weighing, mixing, and pressing of samples into targets. Initially, carbonate and metal powders were weighed into a 6mm x 40 mm Pyrex test tube and then combined using a vortex mixer before transferring the mixture to a pre-drilled sputter target. We later found that the sample could be transferred more completely by weighing carbonate and metal powder onto a square of weigh paper, mixing the sample by doubling the paper and rolling the paper to mix the sample in the resulting trough. The sample was then transferred to a weighed target cartridge, allowing a titanium powder “cap” to be weighed directly on top of the sample. Finally, to allow more effective weighing and eliminate transfer losses with extremely small samples, we tried weighing metal powder, carbonate and cap directly into target cartridges. After weighing and transfer to target cartridges, the samples were compressed to a pellet in the

cartridge using a hammer and drill blank and loaded into a sample carousel with graphite standards and machine blanks.

2.4. Sample measurement

Samples were analyzed using the compact AMS system at NOSAMS [15]. The ion source was a 134 sample MC-SNICS (NEC) which has been modified for improved performance and better vacuum pumping conductance [16, 17]. Carbonate samples were measured in the same manner as graphite samples. Five to ten measurements were made for each sample. Each measurement continued for three minutes or until 30,000 ^{14}C atoms were counted. Carbon ion beam production from targets is measured as $^{12}\text{C}^-$ ion current at the offset low energy Faraday cup after the 90° injector magnet, and these values are given as beam current averaged over all measurements of a target, unless otherwise specified. The data were normalized to graphite NIST OX-I or OX-II targets following the methods of Stuiver and Polach [18] and represented as Fm. Standards were used at the rate of one standard to every 5 carbonate unknowns. Fm is defined as the ratio of the activity of a sample to the activity of an OX-I standard, both normalized for mass dependent fractionation using the $\delta^{13}\text{C}$ of the sample being analyzed. Raw and corrected ratios for carbonate targets indicate that this correction does account for most of the fractionation inherent in the new method. While normalizing carbonate using graphite OX-I standards worked well for determining the performance of targets and quality of data relative to graphite during method development, we intend to develop carbonate normalizing standards for future work.

109 3. Results / Discussion

110 3.1. Method refinement

111 Initial investigations of carbonate sputtering focused on determining whether
112 repeatable measurements could be made and on increasing the ion current produced by
113 carbonate targets. Increases in ion current are correlated to better precision and accuracy
114 of measurement (figure 2). While this relationship is expected due to reduced numbers of
115 counts for low-current samples, variance and bias beyond that predicted by counting or
116 internal error within runs of a sample is apparent at all currents. The extra variance in
117 ratios is possibly due to a combination of heterogeneity in the samples, variability in the
118 amount and composition of the blank, or variability introduced in sample preparation and
119 pressing. We have not fully investigated the source of this variability and the increased
120 variability at low currents, but will do so in future work.

121 As described in the methods section, the first parameter tested was the presence
122 and type of metal powder mixed with the samples. These tests showed that carbonate
123 samples without metal powder produced unusably low currents ($<0.4 \mu\text{A}$), and that
124 samples with titanium powder produced 6 times more current than samples mixed with
125 iron. This agrees with data from Middleton et al. [8] which shows that performance of an
126 early hybrid solid-gas negative-ion Cs-sputter source was directly related to the gettering
127 potential of the metal frit used as a sputtering substrate, and that titanium was the best
128 material. We suspected that the grain size of carbonate and metal powders controls
129 reaction rates via available surface area and/or controls the movement of gaseous reaction
130 products by the size of interstitial spaces in the target. However, tests of different

titanium powders determined that the coarser 100 mesh powder produced the same ion yields as 325 mesh powder within measurement error.

Subsequent tests examined the effect of target size and ratio of carbonate to titanium powder. The best ion currents and precision were obtained with 0.5-1.5 mg carbonate powder and ratios of carbonate to titanium from 0.75:1 to 1.5:1 by mass (figure 3). Adding a titanium “cap” to the sample to act as a sputtering surface improved ion current and measurement precision in some cases. In keeping with the idea of hybrid gas ion source as an analogue for the carbonate sputtering process, the titanium cap may provide more reactive surface area and increase the production efficiency of C^- from CO_2 .

3.2. Performance of carbonate targets

We tested the ion production over time and ionization efficiency of carbonate sputtering by running samples to extinction. Compared with graphite targets, current from carbonate samples rises much more slowly, taking roughly 10 min. to reach full output (figure 4). After an initial warm up (~1-2 min.), relatively stable $^{14/12}C$ ratios are maintained until the ion current drops sharply as the target is exhausted. We measured ionization efficiency by comparing the number of ^{12}C atoms in the sample to the number of $^{12}C^+$ ions reaching the final Faraday cup during the period of stable ratios. After correcting for the transmission efficiency of the accelerator and beam transport (previously estimated at 41% and 98%, respectively), we estimate the efficiency of ion extraction as 8%, compared to 25% for graphite samples tested under similar conditions [16].

A low-energy magnet scan shows the range of negative ions produced by carbonate samples as compared to graphite. We increased the magnet field from 3 kG to

8.5 kG while measuring currents at the off-axis Faraday cup at the accelerator entrance (figure 5). The most notable differences of carbonate samples relative to graphite are reduced $^{12}\text{C}^-$ production, a large $^{16}\text{O}^-$ beam, lack of $^{12}\text{C}_2^-$, and presence of a peak possibly corresponding to CaH_3^- . We examined targets with an optical microscope before and after exposure. After a typical ~ 30 min. run, targets were partially eroded with mottled grey and black deposits. Titanium “capped” samples did not typically appear to have been sputtered through the cap.

The carbonate sputtering method currently has an important drawback. Depending on running conditions, a coating forms on surfaces in the ion source which limits the number of carbonate sample which may be run before the source must be serviced. We have not found reports of similar problems with titanium frit hybrid gas ion sources built around similar sputtering geometry. We hope the problem can be solved by reducing erosion of the titanium front surface of the target during sputtering by replacing the powdered titanium “cap” with a pre-formed frit or solid titanium disk with channels to allow gas transfer to the target surface.

3.3. Measurement quality

To assess carbonate sputtering as a measurement technique, we chose a subset of data meeting the following criteria: 0.4-1.5 mg carbonate mixed with titanium, having a titanium powder “cap” and producing more than $6\text{ }\mu\text{A}$ of $^{12}\text{C}^-$ current. Except as noted, the following sections all use this selected dataset. Where means are compared, we used Welch’s two-sample t-test assuming unequal variances, with results reported as “ $t(N) = T, p = p$ ”, where N is the degrees of freedom, T is the T statistic, and p is the probability that the null hypothesis (means are equal) is false.

3.3.1. Blank correction

Radiocarbon-dead carbonates run by the carbonate sputtering method show that there is a significant contaminant blank present in this method and that this blank is larger than that of the same samples measured as graphite (Figure 6). The blank has a number of potential sources, including the titanium powder, atmospheric CO₂ adsorbed into the carbonate, and carbon contaminant in the carbonate powders. Tests of targets containing only titanium powder produce ¹²C⁻ ion currents of 0.35 μA (SD = 0.26 μA, n = 11), which is 2% of the mean current of carbonate targets but higher than currents from aluminum or iron. The elevated current from titanium could be due to adsorption of CO₂ from air. Comparison of Carrera marble (C1) and a radiocarbon-dead coral (zap-04) show a much larger blank in the coral, similar to the results of Eltgroth et al [19], which used the same coral in a study using graphite. This variable blank complicates the application of a single blank correction based on radiocarbon dead mineral with a low blank because blank corrections must assume that blank is added equally to unknowns and to the standards used in blank correction.

We tested two methods for evaluating and correcting the contaminant blank in carbonate samples. The first method compares Fm values from carbonate sputtering to Fm of (previously) blank-corrected data from the same sample suite run as graphite and uses the linear Fm dependence of this shift to extract the mass and Fm of a blank contribution common to any sample being sputtered as carbonate. The Fm dependence of the shift in Fm error can be seen in Fig. 7a. The negative slope implies a blank addition which adds positive bias at low Fm. When samples have the same Fm as the blank, there should be no bias, assuming no bias inherent in the method. Based on these observations,

the size of the blank is related to the slope of the regression, and the F_m of the blank should be the intercept with the x-axis. This method estimates the mass of the blank as 0.6 $\mu\text{g C}$ (SD = 0.3), with a F_m of 1.30 (SD = 0.8). This method is derived from Bland and Altman's work [20] showing the bias of a new method by showing the difference in methods being compared as a function of the dependent variable.

The second blank correction method is a simple mass balance method using measurements of radiocarbon-dead samples to establish the blank [14]. If the contaminant blank is assumed to be modern and present in all samples equally and all samples are similar in mass, the average F_m of the dead carbonate may be subtracted from unknowns and then scaled such that the full blank is subtracted from dead samples, giving them a corrected F_m of 0, and nothing is subtracted from modern samples, giving them an F_m of 1 (equation 1).

$$(1) F_{m_c} = (F_{m_u} - F_{m_b}) / (1 - F_{m_b})$$

Carbonate data corrected using this method are shown in figure 7b. We chose to use this method for our estimates of the precision and accuracy of carbonate sputtering because it may be easily applied to any suite of unknowns, so long as dead carbonate blanks are included with the samples, while the regression-based method requires a minimum of two standards of differing F_m .

3.3.2. Precision and accuracy

Precision and accuracy of the method were assessed using data from a suite of corals and carbonate standards, selected as described previously. We examined these data before and after applying blank corrections using the second method discussed above. Number of samples, weighted mean and standard deviation for each sample type are

listed in table I, before and after applying the blank correction, and in comparison with the same sample types analyzed as graphite at NOSAMS. In general, carbonate sputtering is less precise than the hydrolysis method. Standard deviations by sample type for corrected data range from 0.0020 Fm for C1 to 0.0094 Fm for the zap-01 coral. The range of deviations for samples run as graphite was 0.0008 Fm for C1 to 0.0087 for zap-01. Standard deviation for the UCI coral standard (CSTD) was 0.0007 when run as carbonate, but this is likely not a reliable statistic. No carbonate sample from this dataset deviated by more than 0.018 Fm from the mean of samples run as graphite.

Examining the distribution of individual sample types provides further insight into the behavior of carbonate sputtering with differing sample composition. Certain sample types (zap-02, zap-04, C2) group with samples of the same type, but have a positive bias relative to graphite. This result implies that all samples do not share a single blank addition of set mass and Fm, or that sample composition affects the sputtering process. The additional blank present in these sample types may be due to organic contamination which is removed by traditional cleaning and hydrolysis, but which remains in the sample and contributes carbon during sputtering of the carbonate. This effect may be mitigated by better cleaning procedures prior to target preparation, or could be controlled for by careful assessment of the organic material present in a suite of samples.

Any systematic bias with the carbonate method is made apparent by examining difference of samples when run as carbonate and graphite as a function of Fm. The slope of a linear regression through these data shows bias related to Fm, while the y-intercept is related to constant bias for all samples. Figure 7 shows that there is little overall bias to the method, and the blank correction accounts for all of the proportional bias and much of

the constant bias. Before blank correction, the weighted mean difference of all selected data from values when run as graphite is 0.005 Fm (SD = 0.007, n = 38). After blank correction, this mean decreased to 0.002 Fm (SD = 0.006, n = 38), not significantly different from zero constant bias (one-sample $t(37) = 1.9$, $p = 0.07$).

We compared agreement of carbonate data with graphite data for each sample type using a two-sample t-test assuming unequal variances as an estimate of agreement between the hydrolysis-graphite and carbonate sputtering methods. With the exception of the zap-02 coral (two-sample $t = 3.5$, $p = 0.01$), the means of samples run using the direct carbonate sputtering method did not differ significantly (p values > 0.05 , see table 2) from means of the same sample type when analyzed as graphite.

Observed scatter between samples of a type is often larger than within-sample measurement error. This can be accounted for by heterogeneity in sample composition; since samples are mixtures of powders, performance may be affected by distribution and size of Ti and carbonate grains within the sample. This is seen to a lesser extent with graphite targets. Estimates of the precision of an individual measurement will only be a predictor of repeatability across multiple samples of the same material if samples and preparation are perfectly homogenous.

3.4. Small Samples

It is worth noting that optimally-sized carbonate targets (750 μg carbonate or 90 μg C) are within the realm of small-sample AMS run at NOSAMS and elsewhere. Preliminary tests of the performance of ultra-small carbonate samples showed promising results. Samples containing as little as 60 μg carbonate (7 μg C) produced better than 4 μA of $^{12}\text{C}^-$ current. The currents from samples containing 7-15 μg C were also relatively

stable over the course of 10 runs lasting 3 minutes each, starting at a mean current of 6 μA rising to a mean peak current of 10 μA before falling to a mean final current of 5 μA . These smallest samples tested had increased internal error due to reduced count rates and increased between-sample error possibly due to variability of blank contribution or increased effect of any heterogeneity of the source materials. Coral standard samples in this size range had a mean F_m of 0.9267 and SD of 0.0109 ($n = 3$), and a two-sample t -test shows that the mean small sample F_m is in agreement with the mean for this standard run as graphite ($t(2) = 2.3$, $p = 0.14$). Two small C1 samples show that blank is elevated for extremely small samples ($F_m = 0.0549$, compared to 0.0075 for large carbonate C1's).

4. Conclusion

We developed a method for the rapid analysis of carbonate samples via AMS by producing carbon ions directly from carbonate in a cesium sputter source. The best results were obtained from 0.4-1.5 mg carbonate powder mixed with 0.5-2.5 mg titanium powder and with an additional 0.5 mg titanium powder "cap" at the front of the target. Samples with this composition generally produced 10-20% of the current of optimally sized (0.5-1.0 mg) graphite targets. Disregarding samples with low current, modern ($>0.8 F_m$) samples have a between sample standard deviation of 0.009 F_m or less. Means of sample types tested are not significantly different than means when samples are run as graphite, with the exception of one sample type. Given the potential for sample dependent bias, limited number of samples in this study, and ongoing development of the method, we conservatively estimate that near-modern samples run using the carbonate sputtering method should agree with values from traditional analysis to within 2%. The

292 technique also holds promise for ultra-small carbonate samples, producing current from
293 samples containing as little as 7 μg C.

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7. Tables

Table I. Summary statistics for sample types used in this study.

Sample type	Description	Graphite			Carbonate				
		n	Fm	sd	n	Fm	sd	Uncorrected Fm	Blank corrected sd
CSTD	UCI coral standard	29	0.9413	0.0024	3	0.9421	0.0007	0.9418	0.0007
zap-01	Deepwater coral	12	0.8816	0.0087	8	0.8782	0.0094	0.8775	0.0095
C2	C2 travertine	29	0.4116	0.0027	3	0.4212	0.0034	0.4180	0.0034
zap-02	Deepwater coral	4	0.2000	0.0031	5	0.2156	0.0062	0.2112	0.0062
zap-03	Deepwater coral	2	0.1535	0.0030	4	0.1640	0.0032	0.1594	0.0032
C1	C1 marble	44	0.0025	0.0008	11	0.0055	0.0020		
zap-04	Deepwater coral	5	0.0038	0.0017	4	0.0165	0.0030		

Table II. Summary of two-sample t-tests for agreement of mean Fm between sample types analyzed as graphite or carbonate.

Sample type	Description	Degrees of freedom	t-statistic	p
CSTD	UCI coral standard	8	0.5	0.65
zap-01	Deepwater coral	14	1.0	0.35
C2	C2 travertine	2	3.0	0.08
zap-02	Deepwater coral	6	3.5	0.01
zap-03	Deepwater coral	2	2.2	0.14

8. Figure captions

Figure 1. (a) Stylasterid coral from West Antarctic Peninsula showing numbered samples for traditional methods that required 4-12 mg of carbonate. Direct sputtering methods may allow dating of individual bands that are highlighted by dotted lines. (b) Foraminiferal tests weighing ~20 µg each.

Figure 2. The relationship of ion current to sample Fm precision and accuracy. The y-axis is the difference of carbonate samples from accepted values for graphite targets producing ~100 µA of $^{12}\text{C}^-$ current, with a value of zero indicating perfect agreement. Triangles and circles are samples with and without a Ti powder “cap,” respectively. Error bars show the greater of error due to counting statistics or one standard deviation of all runs of a target. Lines indicate expected counting error for Fm 0.8 at these currents.

Figure 3. Current produced by carbonate targets compared to (a) the mass of carbonate powder used and (b) the ratio of carbonate to Ti powder by mass. Currents are normalized to current from graphite samples for each run to eliminate differences in AMS system performance between runs. Triangles and circles are samples with and without a Ti powder “cap,” respectively.

Figure 4. Performance of a carbonate target over time. Circles indicate average $^{12}\text{C}^-$ current for each 210 s measurement of a single carbonate target. Squares are raw $^{14}/^{12}\text{C}$ ratio for these measurements, with errors due to counting statistics indicated by error bars. The horizontal line indicates the mean of all measurements.

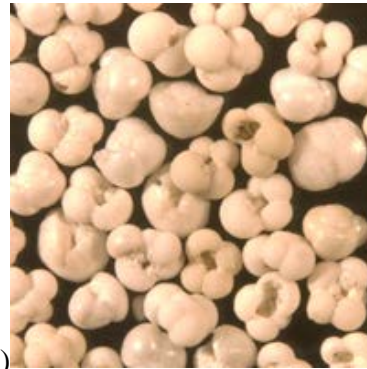
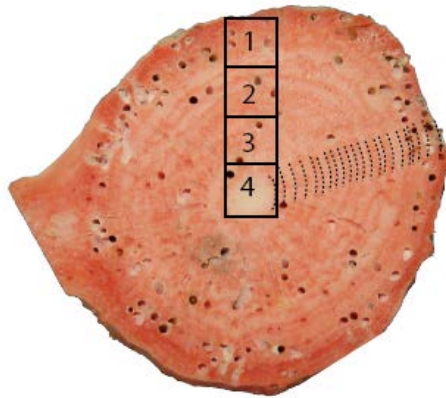
Figure 5. Mass scans of graphite (a) and carbonate (b) targets, produced by measuring ion current at the offset Faraday cup while increasing magnet current.

Figure 6. Comparison of blank carbon for carbonate sputtering and hydrolysis-graphite, grouped by sample type. Boxes and whiskers represent the distribution of the data where the central line is the median, edges of the box are the 1st and 3rd quartiles, whiskers are 1.5 times the inner quartile range, and lone points are outliers. C1 is radiocarbon-dead carrera marble representing 11 and 44 measurements of carbonate and graphite, respectively, and zap-04 is a radiocarbon-dead deep-sea coral with 4 measurements as carbonate and 5 as graphite.

Figure 7. (a) Difference of carbonate samples from accepted values for graphite vs carbonate Fm. Error bars show the greater of error due to counting statistics or one standard deviation of all runs of a target. The grey line with negative slope is a linear fit to the data, and the horizontal line is the mean of all data. The same data with a blank correction applied as described in the text are shown in (b). The horizontal grey lines represent the weighted mean and one weighted standard deviation of these data.

1 9. Figures

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3 a)

b)

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5 1.

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7 Remaining Figures submitted as EPS or PDF files

